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INSTRUMENTS AND METHODS

Effect of selected calculation routines and dissociation constants on the determination of total carbon dioxide in seawater

M. H. C. STOLL,* J. W. ROMMETS* and H. J. W. DE BAAR*

(Received 6 April 1990; in revised form 27 May 1992; accepted 29 May 1992)

Abstract—During the 1989 and 1990 JGOFS North Atlantic Pilot Study a comparison was made between the Coulometric and the acid titration method for determination of total carbon dioxide (TCO_2) in seawater. TCO_2 and alkalinity have been calculated from acid titration using either the modified Gran plot or the curve-fitting routine. Depth profiles showed fair agreement (on average 0.6% or about $12.5 \mu\text{mol l}^{-1}$) between the TCO_2 calculated from the acid titration method and the TCO_2 measured independently by Coulometry. It is shown that different data processing routines combined with the proper use of dissociation constants can influence the acid titration result considerably. There appears to be a slight offset between calculated and Coulometric data which is smallest when using the combined dissociation constants of HANSSON (*Deep-Sea Research*, **20**, 461–478, 1973) with GOYET and POISSON (*Deep-Sea Research*, **36**, 1635–1654, 1989). No statistically significant difference could be found between the two used calculation methods (Gran plot and curve-fitting). The agreement between the independent methods of Coulometry and acid titration is encouraging and furthermore independent of depth, for this dataset there is no reason for invoking the existence of interfering (organic) protolytes

INTRODUCTION

THE past decades have seen a growing emphasis on investigation of the global carbon cycle (TRABALKA and REICHEL, 1986). An understanding of its past and present variations in relation to climate change (e.g. BARNOLA *et al.*, 1987) is prerequisite for assessing the possible effects of increasing atmospheric carbon dioxide levels (BROECKER, 1987). Several policies for controlling or reducing fossil fuel CO_2 emissions have been advocated (SWART and ROTMANS, 1989). The oceans, in themselves a large reservoir of carbon dioxide, constitute a major sink for fossil fuel carbon dioxide (MOORE and BOLIN, 1986; DE BAAR and STOLL, 1989). Ever since the onset of the industrial revolution (~ 1850 A.D.) some 40% of the fossil fuel CO_2 has been taken up by the oceans, the remaining 60% being responsible for the observed atmospheric CO_2 increase (GOUDRIAAN, 1990). The Joint Global Ocean Flux Study (JGOFS) has, amongst others, as its objective “to determine and understand on a global scale the time varying fluxes of carbon and to evaluate the related exchanges with the atmosphere” (DE BAAR *et al.*, 1989).

The carbon dioxide system in seawater is defined by determination of two of the four

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Table 1. Constants used in the calculation of the CO₂ system

The solubility (α_s) of CO₂ in seawater

$$\ln(\alpha_s) = A_1 + A_2(100/TK) + A_3 \ln(TK/100) + S(B_1 + B_2(TK/100) + B_3(T/100)^2)$$

with \ln = the natural logarithm, TK = temperature (°K), S = salinity (‰), $A_1 = -60.2409$, $A_2 = 93.4517$, $A_3 = 23.3585$, $B_1 = 0.023517$, $B_2 = -0.023656$, $B_3 = 0.0047036$ (after Weiss, 1974)

$$TCO_2 = \alpha_s pCO_2 + [HCO_3^-] + [CO_3^{2-}] \quad (\text{Dickson, 1981})$$

$$K_1 = \frac{[H^+] * [HCO_3^-]}{\alpha_s pCO_2} \quad \text{and} \quad K_2 = \frac{[H^+] * [CO_3^{2-}]}{[HCO_3^-]}$$

total Boron	= $[B(OH)_3] + [B(OH)_4^-]$ (Dickson, 1981) = $4.106 * 10^{-4} * (S/35)$ (Culkin, 1965)
$\log K_b$	= $1030.5/TK + 5.5076 - 0.015469 * S + 1.5339E - 04 * S^2$ (Johansson and Wedborg, 1982)
total fluoride	= $[HF] + [F^-]$ (Dickson, 1981)
$\log KF$	= $7.3E - 05 * (S/35)$ (Johansson and Wedborg, 1982) = 398.1 (Johansson and Wedborg, 1982)
total phosphate	= $[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$ (Dickson, 1981)
$\log KP_1$	= $1093.2/TK + 6.0561 - 0.033577 * S + 3.5776E - 04 * S^2$
$\log KP_2$	= $620.53/TK + 4.5038 - 0.030075 * S + 3.3984E - 04 * S^2$
$\log KP_3$	= 1.62 (Johansson and Wedborg, 1982)
total silicate	= $[Si(OH)_3] + [Si(OH)_4^-]$ (Dickson, 1981)
$\log K_{Si}$	= 3.162E + 09 (Johansson and Wedborg, 1982)
total sulphate	= $[HSO_4^-] + [SO_4^{2-}]$ (Dickson, 1981) = $0.02823 * (S/35)$ (Johansson and Wedborg, 1982)
$\log K_s$	= $747.39/TK - 7.1833 + 0.020234 * TK - 0.0094466 * S + 3.9813E - 05 * S^2$
$\log K_w$	= $3418.5/TK + 2.0735 - 0.012756 * S + 7.8097E - 05 * S^2$ (Johansson and Wedborg, 1982)
Alkalinity	= $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}]$ + $[SiO(OH)_3] + [HS] + 2[S^{2-}] + [NH_3] - [H^+] - [HSO_4^-] - [HF]$ - $[H_3PO_4]$ (Dickson, 1981) with S = salinity (‰) and T = temperature (°K)

measurable variables (pH, TCO₂, alkalinity and pCO₂). With the set of equilibration equations of the system (Table 1) the two other variables as well as the concentrations of CO₃²⁻ and HCO₃⁻ can then be calculated. High precision in assessment of all variables is necessary for budget purposes and flux studies. Here we have chosen to measure on shipboard TCO₂ and alkalinity directly by the acid titration method, in addition TCO₂ was measured independently by Coulometry (JOHNSON *et al.*, 1987). An independent estimate of pCO₂ is possible by gas chromatography (TAKAHASHI *et al.*, 1976) but was not part of this study.

The accurate measurement by acid titration of total carbon dioxide (TCO₂) and alkalinity has been subject of considerable investigation and debate (DICKSON, 1981; BARRON *et al.*, 1983; BRADSHAW and BREWER, 1988a, b; JOHANSSON and WEDBORG, 1982). Despite major improvements in experimental conditions (BREWER *et al.*, 1986; BRADSHAW and BREWER, 1988a, b) uncertainty remains (BRADSHAW and BREWER, 1988a). Here we will compare various calculation methods (curve-fitting or modified Gran plot). Also the selection of appropriate and accurate dissociation constants for carbonic acid is by no means a trivial matter (GOYET and POISSON, 1989; GOYET *et al.*, in press).

Here we report the shipboard comparison of (I) the qualitative analysis of titration data for TCO₂ with two data processing routines in comparison with (II) the Coulometric method for determining TCO₂.

MATERIALS AND METHODS

During the Leg I cruise aboard R.V. *Tyro* of the JGOFS North Atlantic Pilot Study from 31 July until 11 September 1989, 320 samples were collected for determining TCO₂ and alkalinity with the acid titration method and the Coulometric method (only TCO₂). During the Leg III cruise aboard R.V. *Tyro* from 7 April until 31 May 1990, 284 samples in total were collected and analysed with both the Coulometric and the acid titration method.

For the determination of both alkalinity and total carbon dioxide the method described by BREWER *et al.* (1986) was used. For the potentiometric titration a titration cell, with a volume of about 115 ml, was constructed of perspex (acrylic) at the NIOZ instrument workshop. Its design is modified after BREWER *et al.* (1986) and BREWER and BRADSHAW (personal communication). The cylindrical cell is surrounded by a jacket through which water is circulated in order to maintain a constant temperature of $20 \pm 0.02^\circ\text{C}$. The complete apparatus was installed inside an air-conditioned laboratory kept at a constant temperature of $20 \pm 1^\circ\text{C}$. Four ports in the top of the cell are provided for the glass electrode (Metrohm 6.0102.100), the reference electrode (Ag-AgCl type; Metrohm 6.0276.100), a Pt-100 thermometer and a 10 ml volume expansion plunger. A capillary tube with anti-diffusion tip supplies acid for the titration. The cell is stirred with a magnetic stir bar. The acid, 0.1 M HCl, fortified to the ionic strength of seawater with 35 g of NaCl, is added from a 10 ml motor burette (Metrohm 665). The millivolt response of the cell was measured with a pH meter (Metrohm 654). Two titrator systems were used simultaneously, under control of a HP 85 computer with a titration programme written by F. EYGENRAAM (NIOZ). Acid was added stepwise in 0.100 ml increments. Readings of mV and ml were stored as data files. Files were processed at the institute using the linear modified Gran functions, in accordance with the algorithms made available by Alvin Bradshaw (WHOI) and the curve-fitting method as described by JOHANSSON and WEDBORG (1982).

Sodium carbonate (Baker analysed reagent) was weighed out by one analyst (Rommets) in approximately 0.25 g lots with a Mettler balance at the institute. The overall weighing error was estimated to be 0.01% or 0.02 mg. These lots were used as the shipboard standards. Standard solutions as well as blanks were made up with 41 g of NaCl in order to match the ionic strength of seawater. The dilution was done shipboard by necessity (BREWER *et al.*, 1986), its volumetric error was estimated at 0.04% for the 1000 ml flask. From these standard determinations the cell volume, blanks and the electrode slope correction factor were calculated. Samples were not poisoned with HgCl₂ as to avoid interferences but analysed as soon as they reached a temperature of 20°C , typically within a couple of hours upon sampling. For converting the results from $\mu\text{mol/l}$ to $\mu\text{mol/kg}$ seawater density was calculated according to the equation given in UNESCO Report no. 44. (UNESCO, 1983).

Samples for the Coulometric method were taken and poisoned with 0.5 ml of saturated HgCl₂ solution (8 g/100 ml) for stabilization during the necessary 6–48 h waiting time until analysis. On reaching room temperature they were then analysed according to the Coulometric method (JOHNSON *et al.*, 1987) with an automatic extractor system built and

Table 2 The four groups of carbonic acid dissociation constants on pH_(SWS) scale and $\mu\text{mol/kg}$ basis

Hansson's constants (Dickson and Millero, 1987)

$$\text{p}K_1 = 851.4/TK + 3.237 - 0.0106 * S + 0.000105 * S^2$$

$$\text{p}K_2 = -3885.4/TK + 125.844 - 18.141 * \ln(TK) - 0.0192 * S + 0.000132 * S^2$$

Mehrbach's constants (Dickson and Millero, 1987)

$$\text{p}K_1 = 3670.7/TK - 62.008 + 9.794 * \ln(TK) - 0.0118 * S + 0.000116 * S^2$$

$$\text{p}K_2 = 1394.7/TK + 4.777 - 0.0184 * S + 0.000118 * S^2$$

Combined Hansson (1973) Goyet and Poisson's constants (Goyet and Poisson, 1990)

$$\text{p}K_1 = 812.27/TK + 3.356 - 0.00171 * S * \ln(TK) + 0.000091 * S^2$$

$$\text{p}K_2 = 1450.8/TK + 4.604 - 0.00385 * S * \ln(TK) + 0.000182 * S^2$$

Original Goyet and Poisson constants (Goyet and Poisson, 1990)

$$\text{p}K_1 = 807.18/TK + 3.374 - 0.00175 * S * \ln(TK) + 0.000095 * S^2$$

$$\text{p}K_2 = 1486.6/TK + 4.491 - 0.00412 * S * \ln(TK) + 0.000215 * S^2$$

TK = Temperature in Kelvin (K), S = salinity in per mille (‰).

supplied by the University College of North Wales at Bangor, UK. Calibration was done according to JOHNSON *et al.* (1987), independently of the acid titration method. The pipette volume was calibrated before and after the cruise with standard solutions of sodium carbonate. The sodium carbonate was taken from a different batch (Baker analysed reagent), weighed out on a different Mettler balance and by a different analyst (Stoll) as the aforementioned standards for the acid titration. The overall weighing error was estimated to be 0.01% or 0.05 mg. The volumetric error was estimated at 0.04% for a 1000 ml flask.

The principle of the analysis is as follows. A very accurate volume of sample is acidified with 8.5% H_3PO_4 (end pH = ~1) and bubbled through by CO_2 -free N_2 gas. The released CO_2 gas is then led to a Coulometer (Model 5011) and back-titrated. For each sample four replicate analyses were executed.

Data of the acid titration method were processed further at the Institute using the newest modified Gran plot (BRADSHAW *et al.*, 1981; BREWER *et al.*, 1986) based upon the program obtained from Dr C. Goyet (WHOI) and the curve-fitting method as described by WEDBORG and JOHANSSON (1982) with a program written after that provided by Dr M. Wedborg (Chalmers University of Technology and University of Göteborg, Sweden). Three sets of dissociation constants were used: those of HANSSON (1973) as also used by JOHANSSON and WEDBORG (1982); those of MEHRBACH *et al.* (1973) and those of GOYET and POISSON (1989). The first two sets (HANSSON, 1973; MEHRBACH *et al.*, 1973) were corrected to the same SWS pH scale as used for the third set (GOYET and POISSON, 1989).

Conversion of carbonic acid dissociation constants to a common basis

The three groups of dissociation constants of carbonic acid ($\text{p}K_1$ and $\text{p}K_2$) are listed in Table 2. They are the results of the work of MEHRBACH *et al.* (1973), HANSSON (1973) and GOYET and POISSON (1989). A direct comparison of the three sets, given a temperature and salinity, is not possible since each author used their own pH scale. GOYET and POISSON (1989) used the now widely accepted pH_(SWS) scale (where SWS means the total hydrogen concentration, a combination of "free" hydrogen ions, HSO_4^- species and HF species), whereas Mehrbach used the pH_{NBS} scale of the National Bureau of Standards. Hansson's

scale is sometimes referred to as pH_{SWS} . However, it is better to write $\text{pH}_{\text{T(Hansson)}}$ since Hansson did not include fluoride in his definition of pH. DICKSON and MILLERO (1987) made a comparison between the dissociation constants of MEHRBACH *et al.* (1973) and HANSSON (1973). From the original titration data they converted both sets to the $\text{pH}_{\text{(SWS)}}$ scale. GOYET *et al.* (in press) did a similar conversion of earlier constants as to compare with the constants of GOYET and POISSON (1989) measured directly on the $\text{pH}_{\text{(SWS)}}$ scale. Latter authors recommended final values for $\text{p}K_1$ and $\text{p}K_2$ that were partly based on earlier assessments of Hansson. These combined sets as well as the original sets of GOYET and POISSON (1989) were used for the calculations in this paper.

Gran method

The calculation of total carbon dioxide and alkalinity from the potentiometric technique with the Gran plot (GRAN, 1952) has been described extensively (DYRSSEN, 1965; BRADSHAW *et al.*, 1981; BREWER *et al.*, 1986). For determination of the equivalence points the concentrations of the nutrients phosphate and silicate have to be known for each sample and were also measured on shipboard.

Briefly, the method is as follows. A data range of about 70 mV is taken just after the anticipated equivalence point. Using the linear least squares regression method the acid volumes V_1 and V_2 required for reaching the first and the second equivalence points, respectively, are calculated iteratively until the difference between the last two calculated values is less than 5×10^{-4} ml. From these two equivalence points, a new data range is estimated, V_1 and V_2 recalculated. This process is repeated until the answer differs by less than $0.5 \mu\text{eq}$ for alkalinity unless the number of range fittings exceeds a predetermined number in which case the sample is flagged as unstable. Similar range fitting procedures had been developed previously by BARRON *et al.* (1983). The method results in a higher regression coefficient for V_1 and V_2 estimates with a consequently more accurate answer. For almost all of the samples, it was noted that fitting the ranges resulted in a stable accurate answer. Unstable (changing) answers were flagged accordingly and omitted in the data sets presented here.

Non-linear curve-fitting procedure

This method as described by JOHANSSON and WEDBORG (1982) and DICKSON (1981) uses least squares minimization of the calculated and experimental values of the dependent variable for all the experimental points and modified Marquardt algorithms. The algorithm used here is described in detail by NASH (1979) and DICKSON (1981). For the calculation, v was chosen as the dependent variable and three adjustable parameters (E_o , A_i and C_i ; JOHANSSON and WEDBORG, 1982) were used.

The program has several enhanced options for analysing a data set. One is the possibility for selecting the maximum number of points of the titration curve to be utilized (which could thus be less than the total number obtained from a titration). Another option is to redo calculations a given number of times, subtracting one data point every time from the data set used. This last option is very useful since it allows detection of ill-defined equivalence points. In such a case results will show a different answer every cycle. In this last case the answer will be flagged as unstable. These answers were omitted from the data

sets presented here. Well defined equivalence points, on the other hand, did yield the same answer almost every time.

PROCEDURE

The acidimetric values of TCO_2 were calculated with two different methods and four different sets of constants. Four sets (1–4) of calculations were made with the Gran plot routine and four sets (5–8) were made with the curve-fitting program.

Gran plots

Set 1 were the calculations done with the dissociation constants of HANSSON (JOHANSSON and WEDBORG, 1982; GHan), set 2 with the dissociation constants of MEHRBACH (1973; GMeh), set 3 with the combined dissociation constants of HANSSON (1973) and GOYET and POISSON (1989; GGPH) and set 4 with the dissociation constants of GOYET and POISSON (1989; GGPORG). All sets relied on the program GRANPLOT.BAS.

Curve-fitting

Set 5 (CHan), 6 (CMeh), 7 (CGPH) and 8 (CGPORG) contained the calculations made with the curve-fitting program CURVEFIT.BAS. For proper comparison between all methods a maximum 275 mV was used since the curvefit program could give erroneous answers if parts of the curve with a pH lower than three is used. With our E_0 of 450 mV we therefore excluded the points with a value of higher than 275 mV (or less if the titration curve had less than this number). The number of cycles (with subtraction of one data point each cycle) was set at two times.

For the choice of the best dissociation constants both programs were given a theoretical data set (JOHANSSON and WEDBORG, 1982) and the results compared with the theoretical answer. Since there was no uniform answer for all the methods we took all four sets of dissociation constants of JOHANSSON and WEDBORG (1982), MEHRBACH *et al.* (1973), combined HANSSON (1973) and GOYET and POISSON (1989) and the original GOYET and POISSON (1989), respectively, for complete comparison (see Table 2).

RESULTS AND DISCUSSION

Examples of typical vertical profiles for alkalinity and TCO_2 distribution are given in Fig. 1. The complete dataset is also available (ROMMETS *et al.*, 1991a,b) on disk. On using the curve-fitting program one should realize that the longer the titration curve is below pH = 3 the more effect it has on the determination of the first equivalence point and thus the calculated TCO_2 value.

With an E_0 of 450 mV we selected 275 mV as a maximum value to be used in the calculations. This results in a typical range of –20 to +275 mV for the titration curve. The option of two successive cycles in the curve-fitting program was used to detect vaguely defined equivalence points. In such a case results would show a different answer every cycle. Well defined equivalence points did on the other hand yield the same answer almost every time.

Sometimes the curve-fitting method would indicate a titration curve to be unstable or

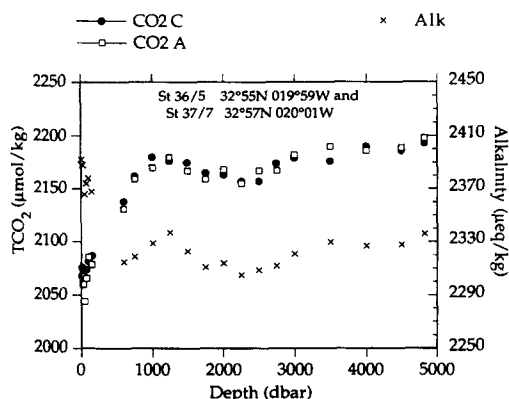


Fig. 1. TCO₂ (Coulometer) and TCO₂ calculated (acidimetric, set 8) and alkalinity plotted against depth (JGOFS I cruise 1989, Stas 36/5 and 37/7).

the Gran plot would give an erratic answer. These are probably not well defined endpoints due to occasionally less than perfect operation of the titrators. On inspecting the flagged (unstable) answers of the four sets calculated with the curve-fitting method, we find that set 5 (Mehrbach's constants) produced two times more flagged samples than set 4, 6 and 8. Apparently for such less accurately measured titration curves the curve-fitting procedure is less stable when using Mehrbach's constants.

From a total of 604 samples collected during the cruises only those in which all four sets could give an unflagged (unstable or erratic) answer for the same sample (a total of 420) are presented here.

The first aim was to find which set of dissociation constants combined with which method (Gran plot or curve-fitting) gave closest agreement with the Coulometric TCO₂ data. For this purpose the calculated TCO₂ obtained from all sets was subtracted from the Coulometric TCO₂ in order to arrive at the difference ΔC . Table 3 lists the eight sets of calculations.

When using the Gran plot it is clear that the constants of HANSSON (1973) yield a somewhat greater deviation from the Coulometric TCO₂ (Table 3). Set 1 shows a higher ΔC than set 2 (Mehrbach's constants). These in turn result in a slightly higher ΔC when compared to the answers obtained with the combined dissociation constants of Hansson and Goyet and Poisson (set 3). Unfortunately the original (measured) constants of GOYET and POISSON (1989) (set 4) show a higher ΔC , which is not easily explained. On looking at the ranges in Table 3 we find that for the first three sets the range is from +25 to -48, but for set 4 the range is +22 to -50, a shift towards the negative side of about 2 to 3 $\mu\text{mol/kg}$, about the difference found between the first three values (~ 4) and the value of set 4 (~ 7). Comparing the four sets, only set 4 has the highest standard deviation. We tentatively conclude that the Gran plot can be influenced substantially by the use of different dissociation constants.

Curve fitting shows the same decreasing trend except for set 6 (Mehrbach). Here we note a surprising positive ΔC compared to all the other negative ones. A close look reveals that for sets 4, 7 and 8 the range varies from $\sim +32$ to ~ -58 but for set 6 from +37 to -47. The shift in range is surprising and for this we have no explanation.

As mentioned previously we have noted that the use of Mehrbach's constants resulted in

Table 3. ΔC (Coulometric TCO_2 – calculated TCO_2) for eight sets

Gran plot (sets 1–4)

- Set 1: Hansson's dissociation constants
- Set 2: Mehrbach's dissociation constants
- Set 3: Combined Hansson and Goyet and Poisson dissociation constants
- Set 4: Original Goyet and Poisson dissociation constants

Curve-fitting (sets 5–8)

- Set 5: Hansson's dissociation constants
- Set 6: Mehrbach's dissociation constants
- Set 7: Combined Hansson and Goyet and Poisson dissociation constants
- Set 8: Original Goyet and Poisson dissociation constants.

Data are in $\mu\text{mol/kg}$ unless otherwise indicated.

	1	2	3	4	5	6	7	8
Number	420	420	420	420	420	420	420	420
Average	–4.2	–4.1	–3.9	–7.1	–7.4	+1.3	–5.4	–3.9
Maximum	25	25	25	22	30	37	32	34
Minimum	–48	–48	–48	–50	–59	–47	–58	–56
Standard deviation	12.4	12.4	12.4	12.8	13.4	13.0	13.6	13.5
Standard error	0.6	0.6	0.6	0.6	0.7	0.6	0.7	0.7

producing about 2 times more unstable answers than sets 5, 7 and 8. On comparing the standard deviation of sets 5–8 (curve-fitting) with those of sets 1–4 (Gran plot) we see a slightly higher standard deviation in sets 5, 6, 7 and 8. We note that the three parameter fit (E_0 , A_t and C_t) tends to give more deviation than the four parameter fit, as advocated by JOHANSSON and WEDBORG (1982). However, the four parameter fit which besides E_0 , A_t and C_t also uses the first dissociation constant of carbonic acid (K_1) as a variable parameter, could not be applied to the data set since one of our purposes is to select the most suitable set of dissociation constants.

Using the Student t test (99% CI, $t = 2.56$) we find for all sets a statistical significant difference between expected (0.0) and found ΔC . A definitive answer as to which set of dissociation constants is best therefore cannot be given. Judging from sets 7 and 8, as compared to sets 3 and 4, the original constants of GOYET and POISSON (1989), e.g. set 8, appear very useful, yet comparable to the combined HANSSON (1973) with GOYET and POISSON (1989) dissociation constants.

We tentatively have chosen latter combined constants for calculating by curve fitting our final values of acidimetric total CO_2 and alkalinity. For alkalinity our values of 1989 and 1990 (ROMMETS *et al.*, 1991a,b) were found to agree very well with results of US colleagues at the same JGOFS stations occupied in the spring of 1989 (SLAGLE and HEIMERDINGER, 1991). The robustness of our alkalinity data was further verified by comparison with alkalinity derived from the same set of constants but now using Gran plots instead of curve-fitting. For the 420 titrations we find the mean difference is $+3.8 \mu\text{eq/kg}$ (Gran–curve fit) with a standard deviation of $5.1 \mu\text{eq/kg}$.

Though systematic differences in ΔC are very small, each individual sample shows a larger difference, varying into both positive and negative direction (Table 3, Fig. 2). It is worth noting that for a given sample the Gran plot as well as the curve-fitting method either both overestimate or both underestimate TCO_2 for the same sample (Fig. 2). When for set

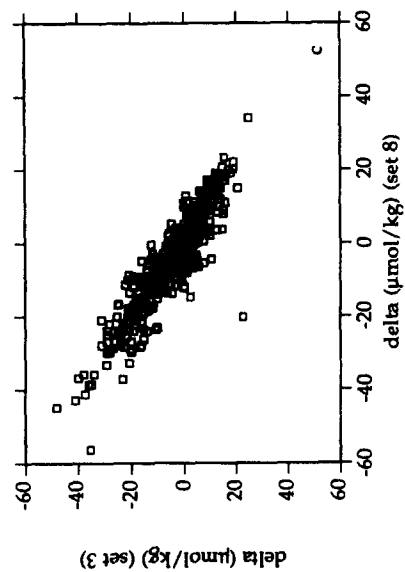
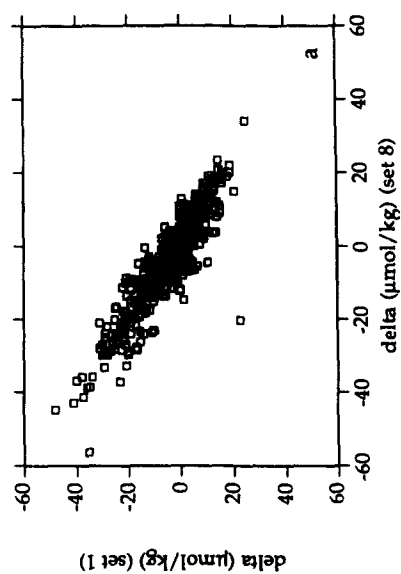
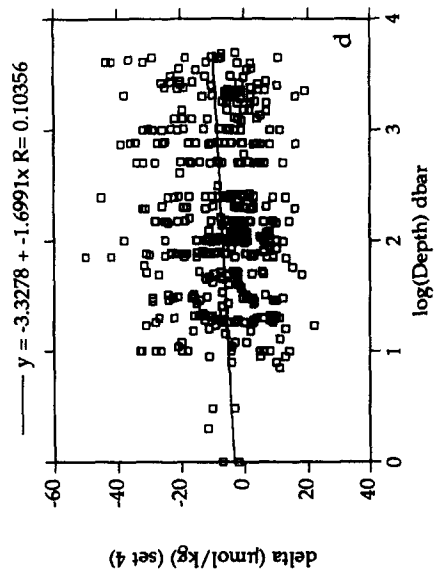
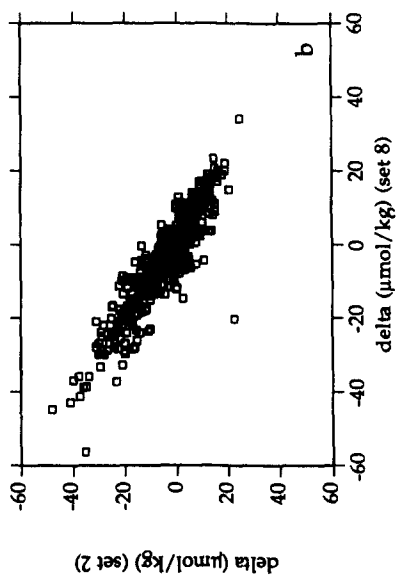
8 the difference ΔC is greater (or smaller) than 0 the ΔC of all other sets (1–7) is also greater (or smaller) than 0. Plotting the ΔC found with the dissociation constants of Hansson (set 5) and set 7 (combined Hansson and Goyet and Poisson) against those of set 8 (original Goyet and Poisson) (Fig. 3e) show almost a straight line whereas the other plots show a rather clouded picture (Figs 3 a–d,f). This is not unexpected since GOYET and POISSON (1989) combined their data with those of Hansson for the first dissociation constant of carbonic acid (K_1). It is this K_1 that dominates the calculated answer so much.

BREWER *et al.* (1986) made mention of the fact that in the TTO data set there appeared to be a systematic offset of $\sim 20 \mu\text{mol/kg}$ between the calculated TCO₂ from the acid titration data and the total CO₂ obtained by gas extraction (Keeling; WEISS *et al.*, 1982). They ascribed the difference to be most likely caused by an inaccuracy in the theory of the potentiometric titration. In a later paper BRADSHAW and BREWER (1988a) discussed the presence of an unknown organic protolyte (HUIZENGA and KESTER, 1979) with a dissociation constant close to that of the first dissociation constant of carbonic acid (K_1). The systematic offset appeared to be the largest in the surface waters, where the recently reported very high DOC levels (SUGIMURA and SUZUKI, 1988) might give rise to higher levels of the unknown organic protolyte. However reproduction of the high DOC values has proven to be difficult (HEDGES, in press; DE BAAR *et al.*, 1992). In the course of the titration the protolyte would hardly affect the alkalinity but would influence the calculated TCO₂ by a substantial amount in masquerading as carbon dioxide. Their measurements on standard solutions (BRADSHAW and BREWER, 1988b) tended to confirm the presence of this, probably organic, acid.

The reproducibility of the Coulometric method is between 1 and $2 \mu\text{mol/kg}$ (JOHNSON *et al.*, 1987). This could explain about $2 \mu\text{mol/kg}$ of the standard deviation of $\sim 12 \mu\text{mol/kg}$ with the remaining $\sim 10 \mu\text{mol/kg}$ to be ascribed to reproducibility of the acidimetric titration and minor errors between the two balances. Latter errors are deemed small ($\sim 1 \mu\text{mol/kg}$) such that the reproducibility of the titration would be about $8\text{--}9 \mu\text{mol/kg}$, substantially less precise than the $\pm 2 \mu\text{mol/kg}$ reported by BRADSHAW and BREWER (1988b). On preparing for our cruise, we took care as to weigh in standards on different balances as to ensure completely unbiased comparison between the two methods. Ironically, our results show that to ensure a comparable dataset it would be better to weigh in standards on the same balance.

The overall gravimetric and volumetric error of the standard solution is estimated at 0.06% for each method, i.e. 0.09% for the difference ΔC between the two methods. This would correspond to a possible error of about $\pm 1.8 \mu\text{mol/kg}$ (at TCO₂ $\sim 2000 \mu\text{mol/kg}$) to be compared with the here found systematic offset in the order of $-7.4 < \Delta C < +1.3$ but likely to be about $-4 \pm 12 \mu\text{mol/kg}$ (Table 3). Obviously latter offset also depends on selected calculation routines and dissociation constants rather than calibration errors of weight and volume alone.

To see whether the apparent discrepancy between (I) the titrations with various calculation methods and (II) Coulometry was dependent of depth (BREWER *et al.*, 1986) we plotted the differences found for each set of calculations against the depth (Table 4). When fitting a line with the least squares regression method we find for all the methods a regression coefficient of about 0.0 and b has a value of 0.0 which shows that the difference is independent of depth. Our sampling strategy, however, had a strong bias towards surface samples. Most of the samples were taken in the 0–1000 m range. To circumvent this problem we plotted the data against the $^{10}\log$ of the depth (Fig. 3). This method gives an



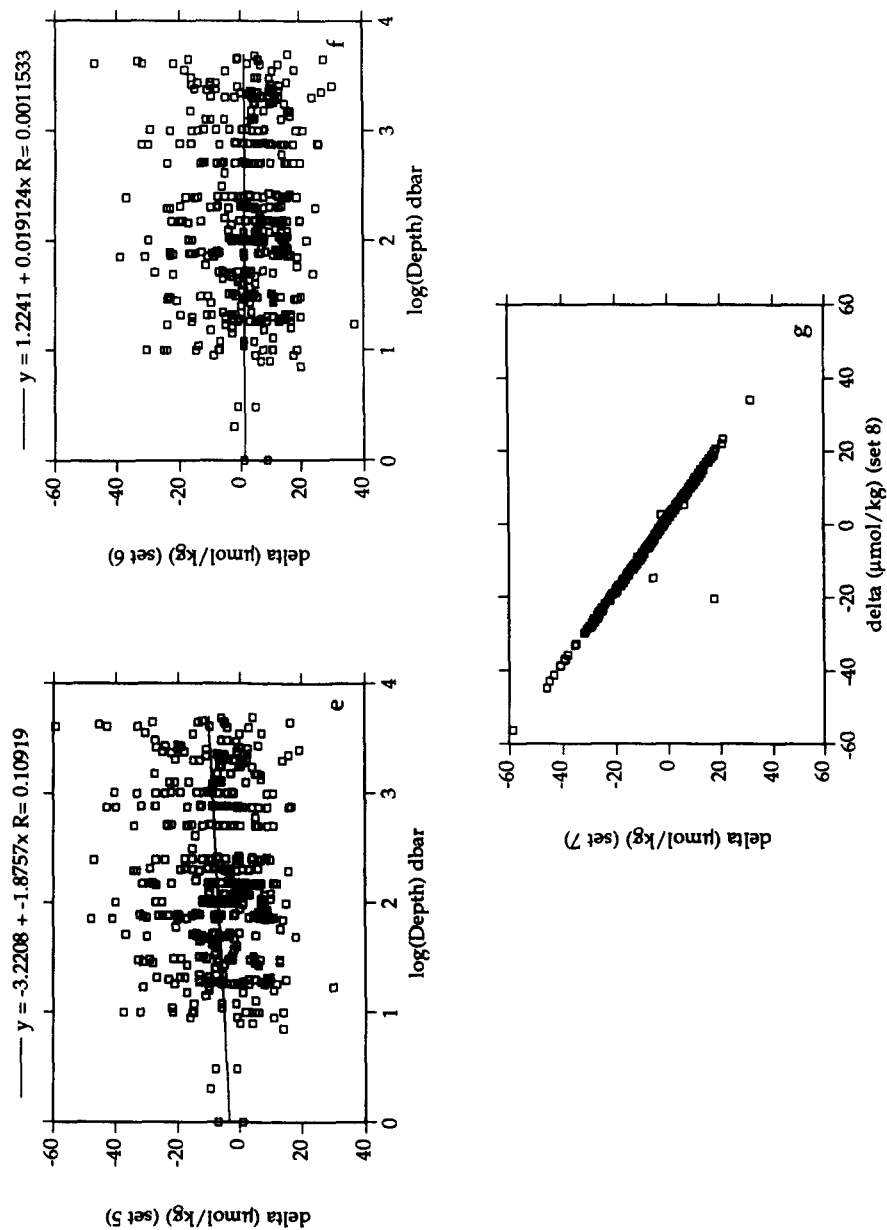
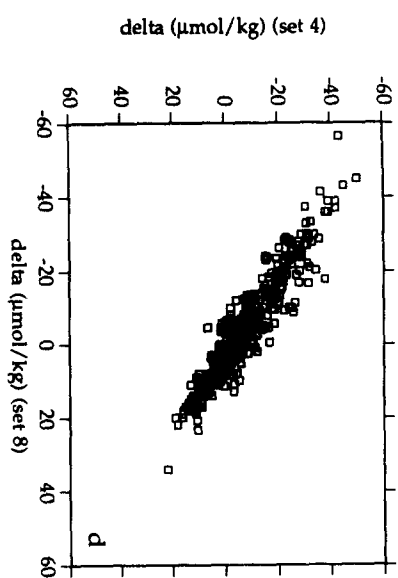
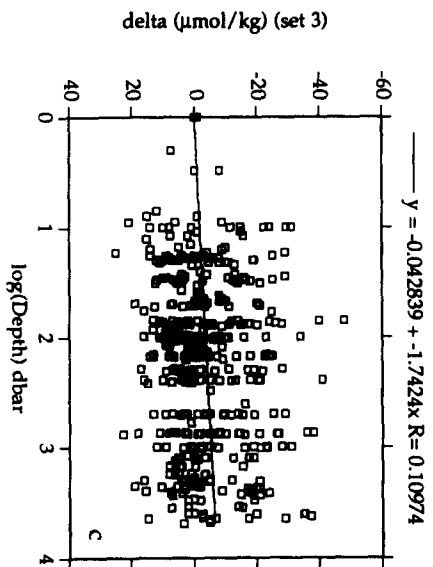
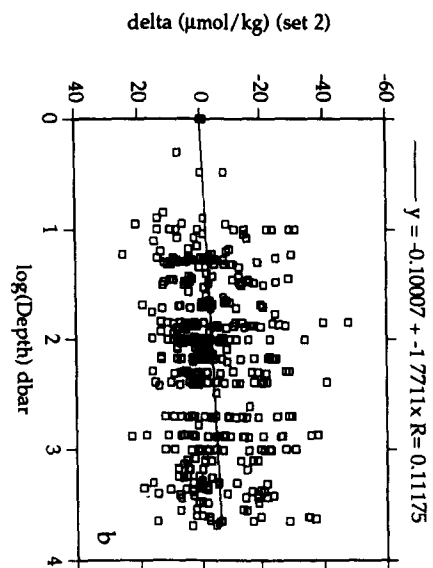
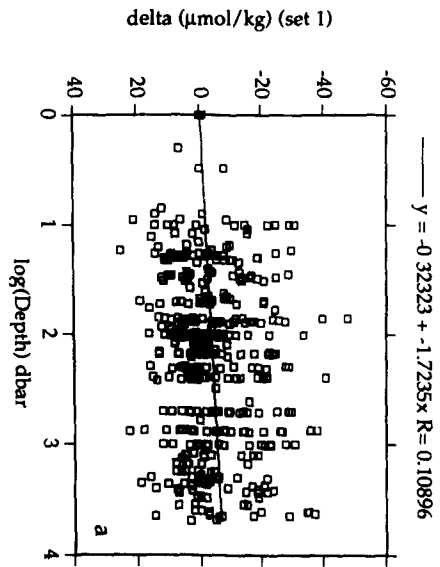


Fig. 2 Plots comparing the difference δC (TCO_2 Coulometric-calculated TCO_2) between methods for the curve-fitting calculation with the original Goyet/Poisson constants (set 8, horizontal axis) vs each of the other calculations (sets 1–7, vertical axis). See Table 3 for definition of each set (1–8).



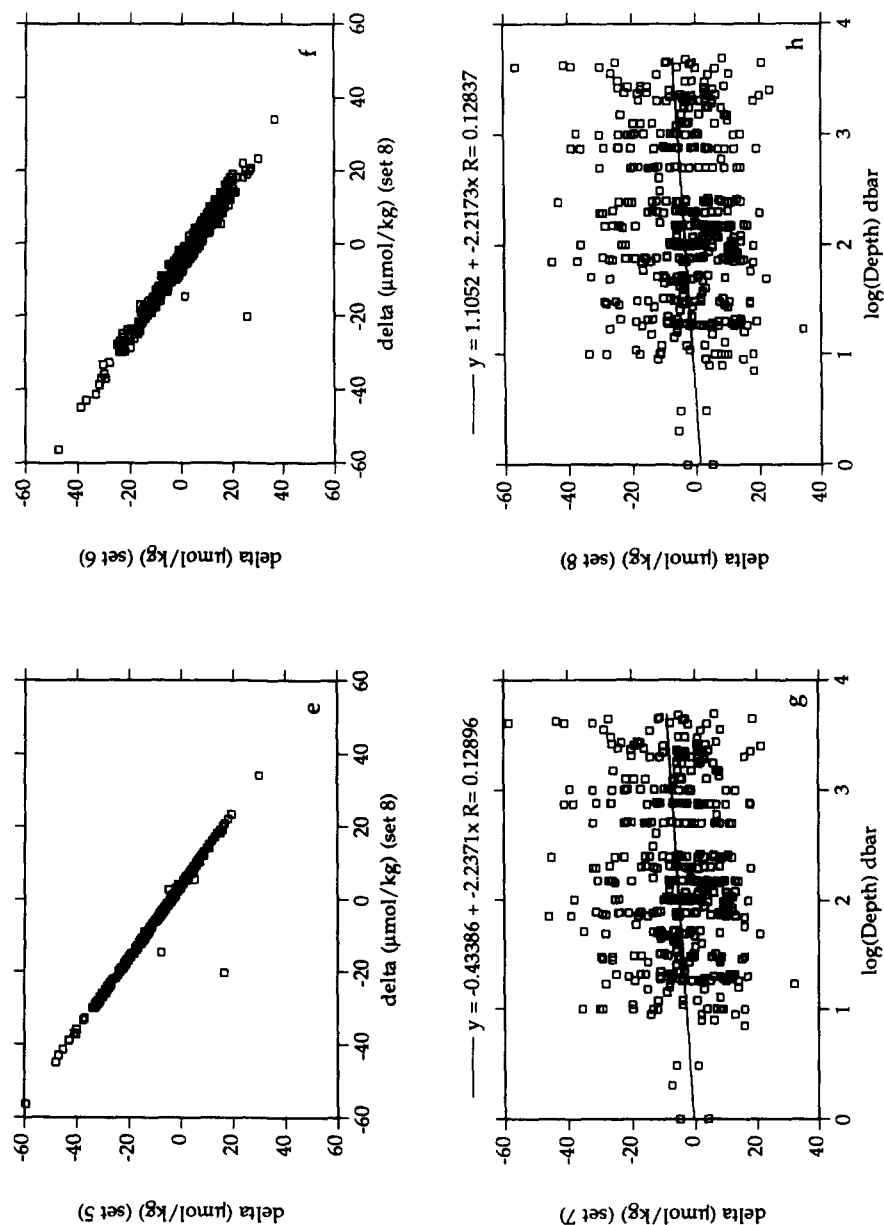


Fig. 3 Plots comparing the difference between TCO_2 (Coulometer) and calculated TCO_2 (deltaC) plotted against the $^{10}\log$ (depth). See Table 3 for definition of each set (1–8)

Table 4. Linear regression for eight sets of calculations

$\text{deltaC} = a + b * \text{depth}$. r = regression coefficient.

Gran plot (sets 1–4)

Set 1: Hansson's dissociation constants

Set 2: Mehrbach's dissociation constants

Set 3: Combined Hansson and Goyet and Poisson dissociation constants

Set 4: Original Goyet and Poisson constants

Curve-fitting (sets 5–8)

Set 5: Hansson's dissociation constants

Set 6: Mehrbach's dissociation constants

Set 7: Combined Hansson and Goyet and Poisson dissociation constants

Set 8: Original Goyet and Poisson constants.

Data are in $\mu\text{mol/kg}$ unless otherwise indicated.

	1	2	3	4	5	6	7	8
a	-3.40	-3.26	-3.15	-6.29	-6.56	1.39	-4.43	-2.91
b	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
r	0.102	0.103	0.102	0.104	0.102	0.019	0.119	0.112

artificial "weighed regression" when using the least squares regression method again. The regression coefficient is still 0.0 for all the methods. We find in all cases (except set 5 and 8: $a \sim 1$) a tendency to underestimate deeper samples and to overestimate surface water samples as compared to the Coulometric TCO_2 . This is just the opposite from the trend reported by BREWER *et al.* (1986), where a similar titration method was compared with gasometric total CO_2 analyses (WEISS *et al.*, 1982). For our limited dataset the acid titration method does not differ systematically from Coulometry for determining TCO_2 in seawater, albeit the inherent precision of Coulometry appears to be superior. Obviously there remains a need for more comprehensive intercalibration between various methods (gasometric pCO_2 , Coulometry, acid titration) and laboratories (DICKSON, unpublished).

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